Evidence of Covalency in Hydrogen Bonding of Liquid Water

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In this work we show a new way to address the long-standing question of hydrogen bonding in liquid water. Chemical reactions taking place in liquid water are essential for many important processes in electrochemistry, environmental science, pharmaceutical science, and biology in general. Many models have been proposed to view the details of how liquid water is geometrically organized by hydrogen bond network. A very important but hitherto less addressed question is that of the hydrogen bond effect on the electronic structure. This effect is essential for understanding the physical and chemical properties of many chemical and biological systems. The reason for this neglect, however, is the limited experimental access to the electronic structure of liquids.

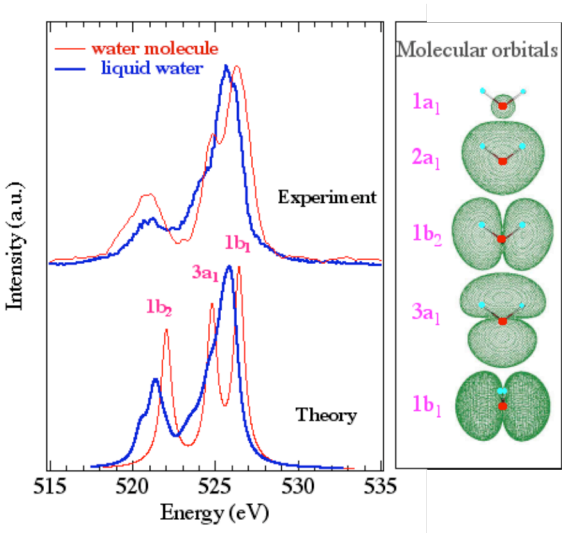

Figure 1. X-ray emission spectra of the water molecules and liquid water, formed as electrons from the three outermost occupied molecular orbitals, schematically depicted in the right panel, fill a vacancy in the $1a_1$ core level. The excitation energy is 543 eV, well above the ionization limit but sufficiently low so that the emission from multiply excited states can be neglected.

We have applied X-ray emission spectroscopy in liquid water to reveal the influence of the hydrogen bonding on the local electronic structure [1]. The X-ray emission spectrum of the water molecule is dominated by transitions from the three occupied oxygen *2p*-derived orbitals, $1b_2$, $3a_1$, and $1b_1$, to the oxygen *1s* orbital, $1a_1$ (Fig. 1). The $1b_2$ and $3a_1$ orbitals, which are oriented in the plane defined by the nuclei, are mainly responsible for the OH bonding, and they mix considerably with the hydrogen orbitals. The $1b_2$ orbital is antisymmetric with respect to the bonds, whereas the $3a_1$ orbital has its nodal plane perpendicular to both symmetry planes of the molecule. The $1b_1$ orbital is the so-called 'lone pair' orbital with the nodal plane coinciding with the plane defined by the nuclear positions. The intensity and the natural width of the peaks in the X-ray emission spectrum reflect the characters of the orbitals.

We found a strong involvement of the a_1-symmetry valence orbital in the hydrogen bonding. The character of $3a_1$ is entirely changed due to the influence of the hydrogen

bonding. From electrostatic considerations it is obvious that both donor and acceptor hydrogen bonds tend to increase the local dipole moment of the molecule. As the $3a_1$ orbital has the nodal plane perpendicular to the direction of the electric dipole moment of the water molecule, it is likely to show the largest polarizability in this direction. Electron density is transferred from the lobe enclosing the hydrogen nuclei towards the oxygen lobe. Here the orbital mixes substantially with the orbitals of the neighboring molecules and its original character is lost. The local electronic structure of water molecules, where one hydrogen bond is broken at the hydrogen site, is separately determined.

Pauling stated that the electron sharing between water molecules results in the covalency in the hydrogen bond. The experimental findings provide the direct experimental evidence that there is electron sharing between water molecules, which confirms Pauling's prediction of covalency in hydrogen bond. However, coordinate-covalent bonding (also called donor-acceptor or Lewis acid-base bonding) is also defined as the sharing of an electron pair of one molecule via an empty orbital of the other. Under this definition, the covalent bond between two water molecules would primarily affect the outmost orbital ($1b_1$). Covalency in this sense is not supported by our experimental results. The present studies provide an illustration of the important potential of X-ray emission spectroscopy for elucidating basic features of liquids.

References:

1. J.-H. Guo, Y. Luo, A. Augustsson, J.-E. Rubensson, C. Såthe, H. Ågren, H. Siegbahn, and J. Nordgren, "X-ray Emission Spectroscopy of Hydrogen Bonding and Electronic Structure of Liquid Water", Phys. Rev. Lett. **89**, 137402 (9 September, 2002).

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